LONG LIFE NICKEL ELECTRODES FOR A NICKEL-HYDROGEN CELL: CYCLE LIFE TESTS

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INTRODUCTION

Nickel electrodes have been recognized as the life-limiting components of nickel-hydrogen cells. In order to develop a long life nickel electrode for a nickel-hydrogen cell, we are engaged in studies of various parametric effects on the electrode cycle life. These parameters include plaque pore size, plaque mechanical strength, and active material loading level. Three levels of variation were used for each parameter. Several fabrication parameters of nickel plaques, including nickel powder type, powder density, and sintering time were studied in order to fabricate plaques with desired parametric variation (1). Selected plaques (7 types) were impregnated in three levels of active material loading using the standard Air Force/ Hughes electrochemical deposition process in an alcoholic bath. Subsequently, these electrodes were tested by a Hughes standard test procedure (200 cycles) as a part of their evaluation. For a cycle life evaluation of these electrodes, 19 different nickel-hydrogen boiler plate test cells were fabricated. This initial cell performance has been described earlier (1). The present report presents the results of the cycle life tests of the boiler plate cells. Details of the failure analyses of these test cells will be presented later (2).

TEST CELL MATRIX AND ACCELERATED CYCLE LIFE TEST

The nickel-hydrogen boiler plate test cell matrix includes 19 out of the 21 various designs of electrodes, as shown in Table 1. Each electrode type was designated as follows for convenience of later discussions: The first two digits represent the nickel powder type and the median pore size, i.e., 55 for INCO nickel powder type 255 and 10 μm pore size, 25 for 255 powder type and 16 μm pore size, and 87 for 287 powder type and 13 μm pore size, respectively. The last two digits represent

of these cells initially increased with cycling along with other cells up to about 1000 cycles and then started to decrease, while the pressure of the other cells, on average, either remained constant or increased with cycling.

PARAMETRIC EFFECTS OF CYCLE LIFE

Rated and theoretical capacities (chemical capacity) depth-of-discharge (DOD) of cycling with respect to the theoretical capacity, and the cycle life to 0.9 V of EODV are summarized in Table 2. Although the rated capacity was based on the initial measured capacity, the theoretical capacity was used in the analysis of the results. This is because the measured capacity varied with the measurement conditions and showed a memory effect of prior cycling. The cycle life of nickel electrode depends strongly on the DOD of cycling. Therefore, it is necessary to compare the cycle life of various cells at a given value of DOD in order to evaluate the effects of the electrode parameters. A quantitative relationship between cycle life and DOD of a nickel-hydrogen cell or a nickel electrode is not available. However, the following quantitative relationship between the DOD and an expansion rate of the nickel electrode active material has been established (4).

$$k=A\ (\%DOD)^{2.4} \quad , \qquad (1)$$

where k is the expansion rate and A is a constant. For the present data analysis it has been assumed that the cycle life of the nickel electrode is inversely proportional to this rate, k. The measured cycle life was normalized to 70% DOD of the theoretical capacity using the relationship in Equation (1), combined with this assumption.

The normalized cycle life values are summarized in Table 2 and plotted against the median plaque pore size, the plaque bend strength, and the active material loading in Figures 3, 4 and 5, respectively. The optimum pore size appears to be about 12 μm, regardless of the loading level (Figure 3). The 16-μm plaques showed much shorter cycle life than the other plaques.

mechanical strength (bend strength): 40 for 400 psi, 55 for 550 psi, and 70 for 700 psi. For example, an 8755 plaque is made of 287 type powder with a bend strength of 550 psi and a median pore size of 13 μm. The letters L, M, and H indicate the nominal active material loading levels of 1.4, 1.55, and 1.7 g/cc void, respectively.

All test cells contained three standard flight-type nickel electrodes in a recirculation stack design (3) and 31% KOH electrolyte. The cell capacities were rated in three groups: 2.7, 3.0 and 3.3 A-hr, based on capacities measured by charging the cells for 80 minutes at C rate and then discharging them to 1.00 V at 2.74 C rate. The initial measured capacities ranged from 2.8 to 3.1 A-hr, from 3.1 to 3.5 A-hr and 3.5 to 3.9 A-hr for the 2.7, 3.0, and 3.3 A-hr ratings, respectively.

The cycle life tests of all of the 19 boiler plate test cells were carried out at 23°C by a continuous cycling to 80% depth-of-discharge of their rated capacities using 45-minute cycle regimes. These were interrupted periodically for capacity measurements after approximately every 1500 cycles. The cycling regime included a 2.74 C rate of discharge for 17.5 minutes and a 27.5-minute charge at 1.92 C rate for 110% recharge. End-of-charge voltages (EOCV) and end-of-discharge voltages (EODV), and end-of-charge pressures (EOCP) and end-of-discharge pressures (EODP) of the cells were monitored daily (every 32 cycles).

CELL VOLTAGE AND PRESSURE DURING LIFE TEST

Plots of EODV and EODP of various cells versus the number of life cycles are shown in Figures 1 and 2. The EODV decreased gradually with cycling until near the end of life where the voltage decrease accelerated, except in two anomalous cells; i.e., 8770H (Figure 1) and 5555M (Figure 2). The end of life was defined as 0.9 V of the EODV. The EOCV's of the cells showed neither any appreciable variations with various electrode types nor any appreciable change during the cycle life test.

The EOCP's and EODP's of a given cell changed in parallel to each other as expected by the fixed quantity of charge and discharge. The cells with short cycle life showed overall lower pressure than the other cells. These short life cells, which include the 2540 type and all L-series, also showed a pressure peak. The pressure

No definite effect of the bend strength on the cycle life was identified, due to the spread data points, as shown in Figure 4.

The active material loading level affected the cycle life strongly, as shown in Figure 5, if the values of the 2540 plaques were disregarded because of their exceptionally short life. The optimum loading level appears to be at about 1.6 g/cc void. The preceeding conclusions on the parametric effects on the cycle life did not change when the data were alternatively analyzed using the cycle life values of 0.5 V for the end of life, or without using the DOD correction.

CELL PRESSURE AND ACTIVE MATERIAL UTILIZATION

Analyses of the cell pressures during the interim cell capacity measurements revealed a relationship between the cell pressure and the active material utilization. This utilization is defined as the ratio of the measured vs the theoretical capacities. A normalized cell pressure after full charge and discharge, $(P-P_o)/C_o$, (where P is the cell pressure, P_o is the precharge pressure, and C_o is the theoretical capacity of nickel electrode), is plotted against active material utilization of the cells after 1700 life cycles (Figure 6). The term $(P-P_o)/C_o$ is a measure of the average oxidation state of the nickel active material. After full charge and full discharge of the cell, the plots gave straight lines, respectively. The values of $(P-P_o)/C_o$ at charged state increased, while the values at the discharged state decreased as the utilization increased. The values at the charged state increased more rapidly than those at the discharged state decreased when the utilization increased. This result appears to indicate that an increased active material utilization is more dependent on reaching a high average oxidation state than on discharge to a low average oxidation state. This observation after 1700 cycles is quite contrary to an earlier observation at the beginning of life on the relationship between $(P-P_o)/C_o$ and the active material utilization which showed that the average oxidation state in the charge state was independent of the utilization (1). The utilization was entirely dependent on the oxidation state in the discharged state. It is speculated that this change of the relationship between the utilization and $(P-P_o)/C_o$ with cycling may indicate a change of the mechanism of the active material utilization. The value of $(P-P_o)/C_o$ gradually increased with an increased

number of cycles. This increase appears to be due to either an increase in the average oxidation state of active material or a gradual corrosion of the nickel sinter to be converted to nickel oxides or hydroxides, or both.

CONCLUDING REMARKS

- The active material loading level strongly affects the cycle life of the nickel electrodes, showing the optimum loading level at about 1.6 g/cc void.
- The plaque pore size affects the cycle life significantly, showing that the optimum pore diameter was about 12 μm.
- No noticeable effect of the plaque mechanical strength on the cycle life was found in the bend strength range of 400 to 700 psi.
- As the test cells were cycled, the average values of $(P-P_o)/C_o$ gradually increased, and the relative dependence of these values at the charged and discharged states on the active material utilization was changed, indicating a potential change of the utilization mechanism of active material.

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Table 1. Boiler Plate Test Cell Matrix and Designation of Cell Types.

13285–4R2

	BEND STRENGTH	400 psi			550 psi		700 psi	
	PORE SIZE, μm	10	13	16	10	13	10	13
ACTIVE MATERIAL LOADING LEVEL	1.4 g/cc VOID	* 5540L	* 8740L	* 2540L	* 5555L	* 8755L	5570L	* 8770L
	1.55 g/cc VOID	* 5540M	* 8740M	* 2540M	* 5555M	* 8755M	* 5570M	* 8770M
	1.7 g/cc VOID	* 5540H	* 8740H	* 2540H	* 5555H	* 8755H	5570H	* 8770H

*INCLUDED IN 19 TEST CELLS

Table 2. Summary of the Boiler Plate Cell Cycle Test

13858–4

CELL TYPE	CAPACITY, A–hr		DOD, % WITH RESPECT TO THEORETICAL CAPACITY	MEASURED CYCLE LIFE TO 0.9V	CALC. CYCLE LIFE AT 70% DOD
	RATED	THEO-RETICAL			
8770H	3.0	3.80	63.2	– – –	– – –
8770M	2.7	3.37	64.1	6430	5205
8770L	2.7	3.02	71.5	3440	3620
8755H	3.0	3.62	66.3	4260	3739
8755M	3.0	3.54	67.8	3950	3659
8755L	2.7	3.06	70.6	3520	3593
8740H	3.3	3.79	69.7	4480	4434
8740M	2.7	3.56	60.7	11904	8455
8740L	3.0	3.21	74.8	2870	3365
5570M	3.3	3.58	73.4	3730	4180
5555H	3.3	3.81	69.3	3990	3895
5555M	3.3	3.54	74.6	– – –	– – –
5555L	3.3	3.44	76.7	2720	3387
5540H	3.3	3.81	69.3	3900	3807
5540M	3.0	3.53	68.0	6030	5625
5540L	3.0	3.39	70.8	2660	2734
2540H	3.0	3.44	69.8	2180	2165
2540M	3.0	3.31	72.5	2400	2610
2540L	3.0	3.14	76.4	2060	2541

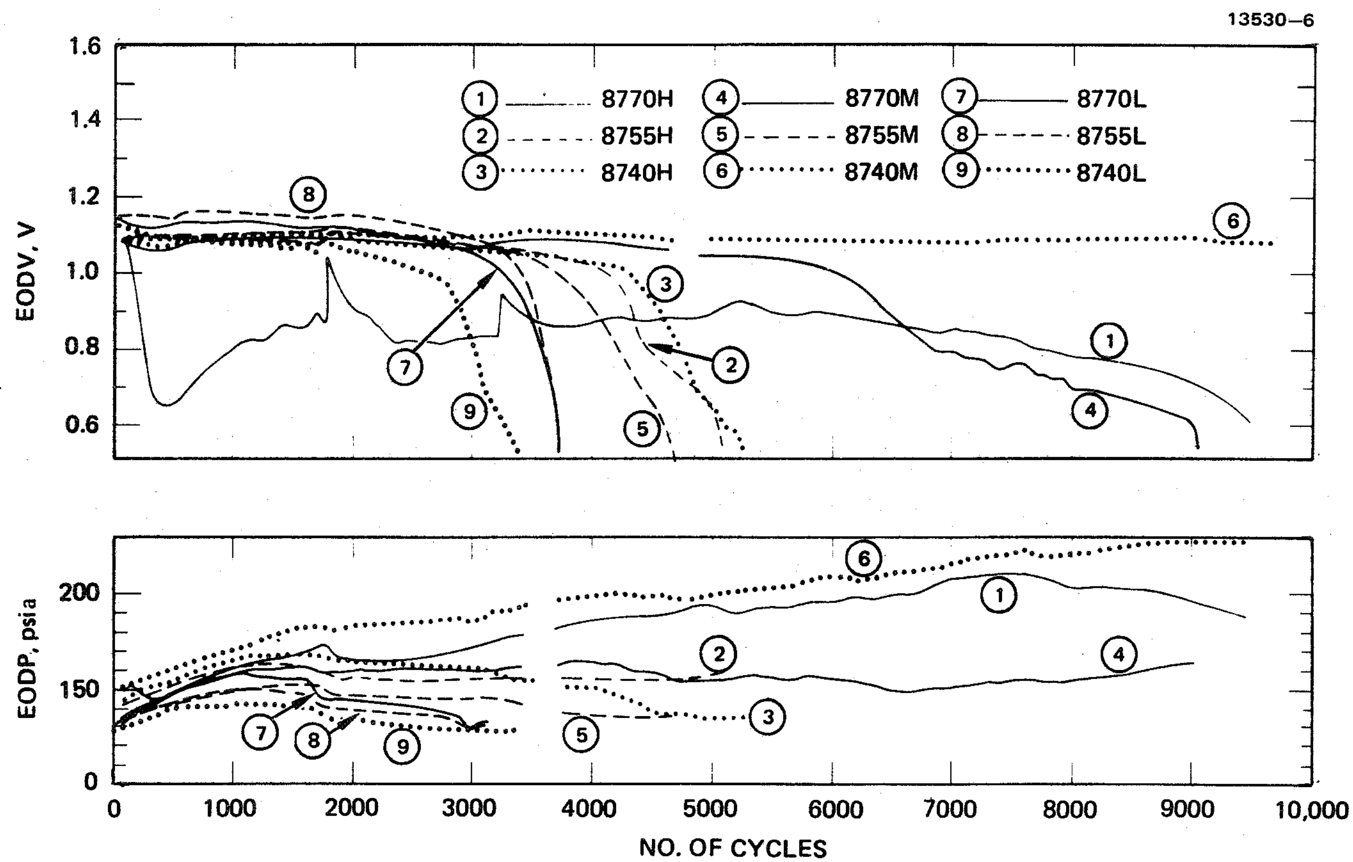

Figure 1. Plots of EODV and EODP versus number of cycles for 87XX electrodes.

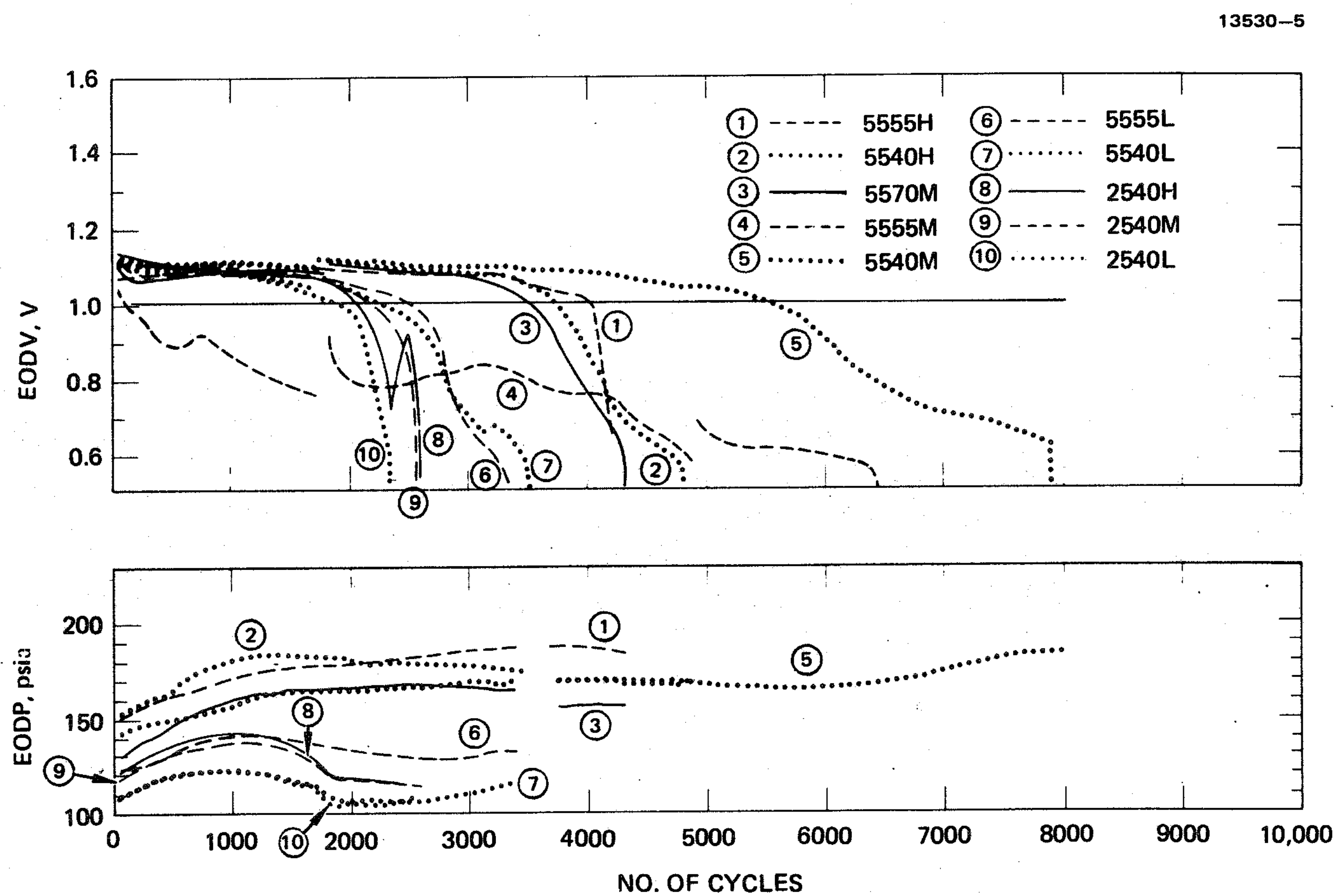

Figure 2. Plots of EODV and EODP versus number of cycles for 55XX and 2540 electrodes.

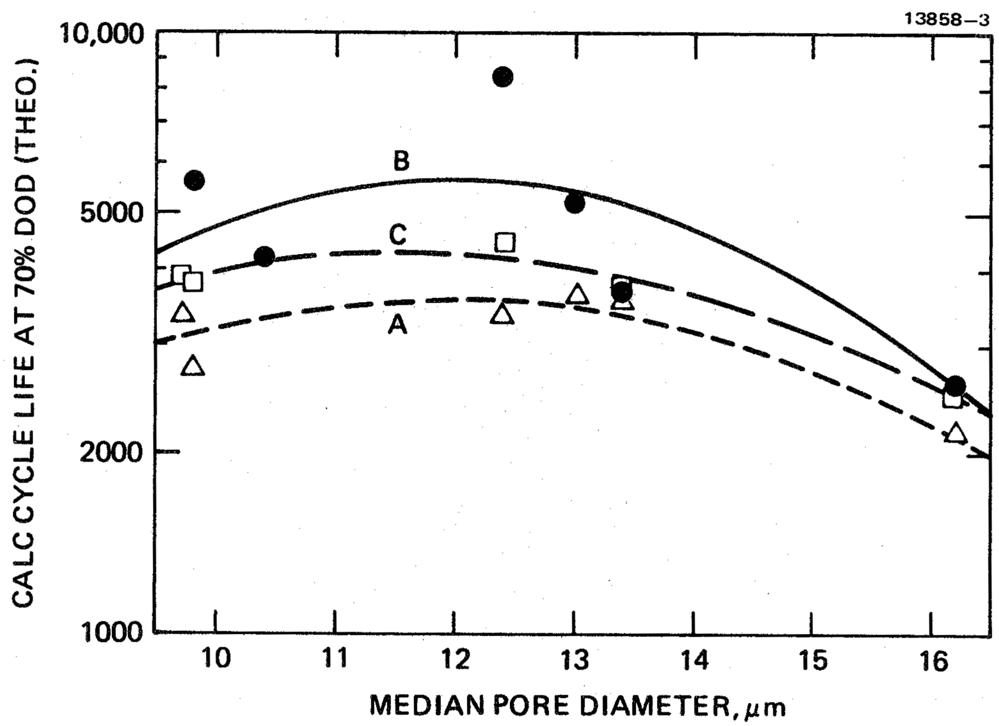

Figure 3. Plots of the normalized (calc.) cycle life at 70% DOD with respect to the theoretical capacity versus median plaque pore diameter. Curves A (Δ), B(●), and C (□) represent active material loading level of 1.4, 1.55, and 1.7 g/cc void, respectively.

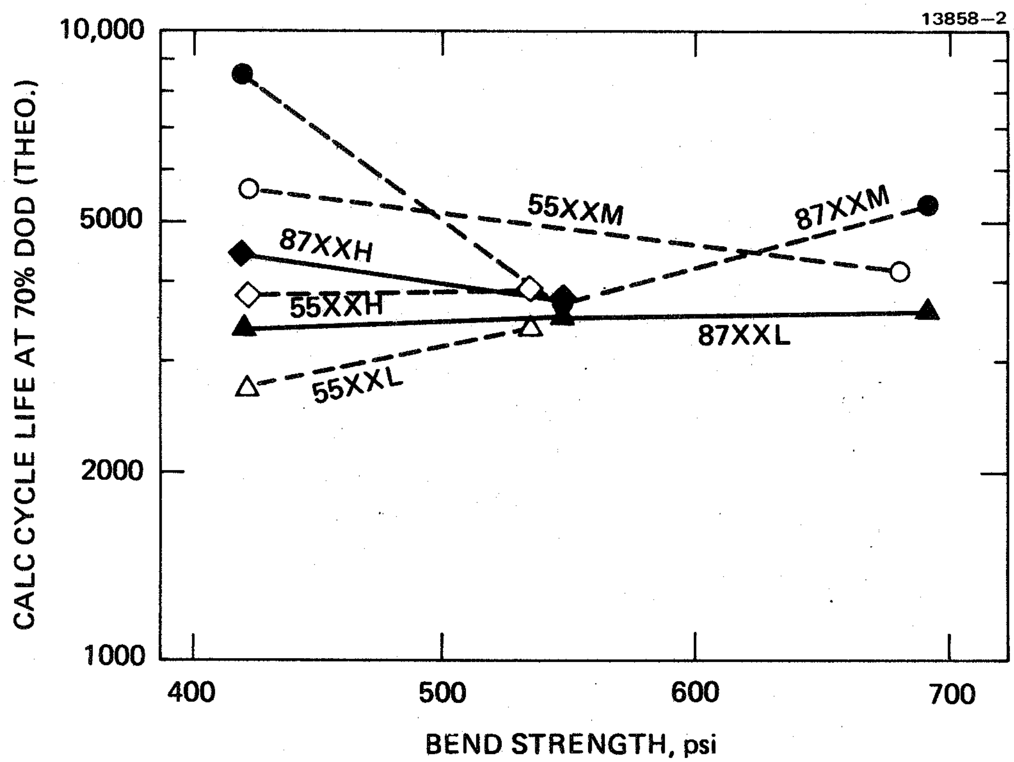

Figure 4. Plots of the normalized (calc.) cycle life vs plaque bend strength for various plaque types and the active material loading level.

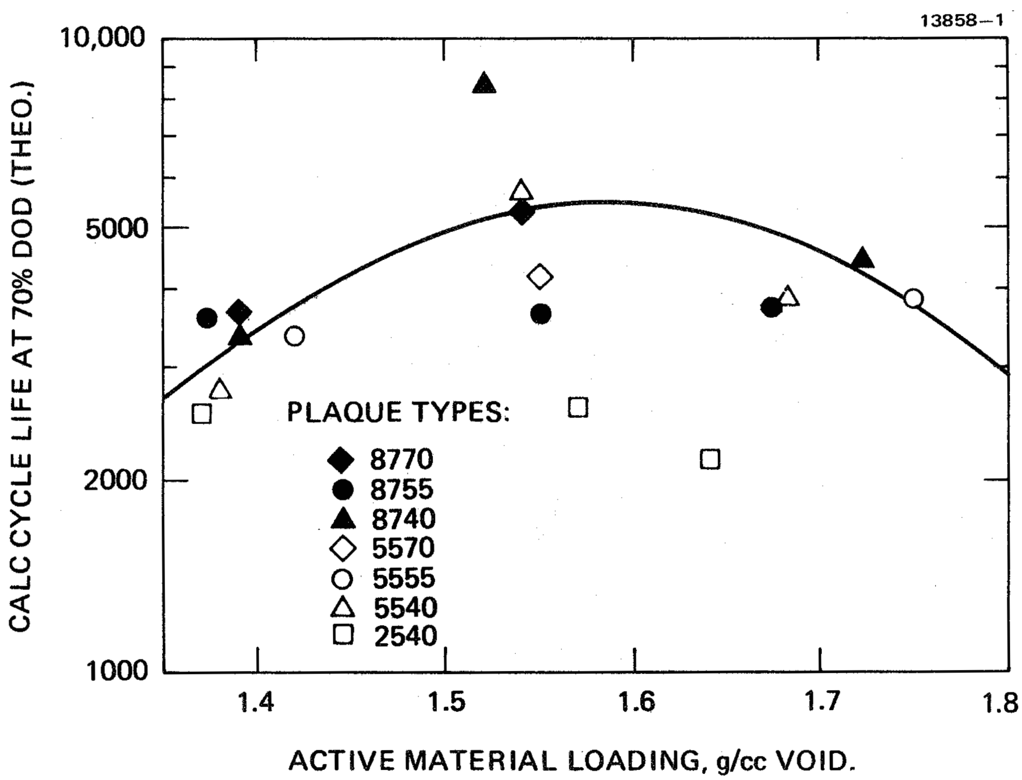

Figure 5. Plots of the normalized (calc.) cycle life vs the active material for various types of electrodes.

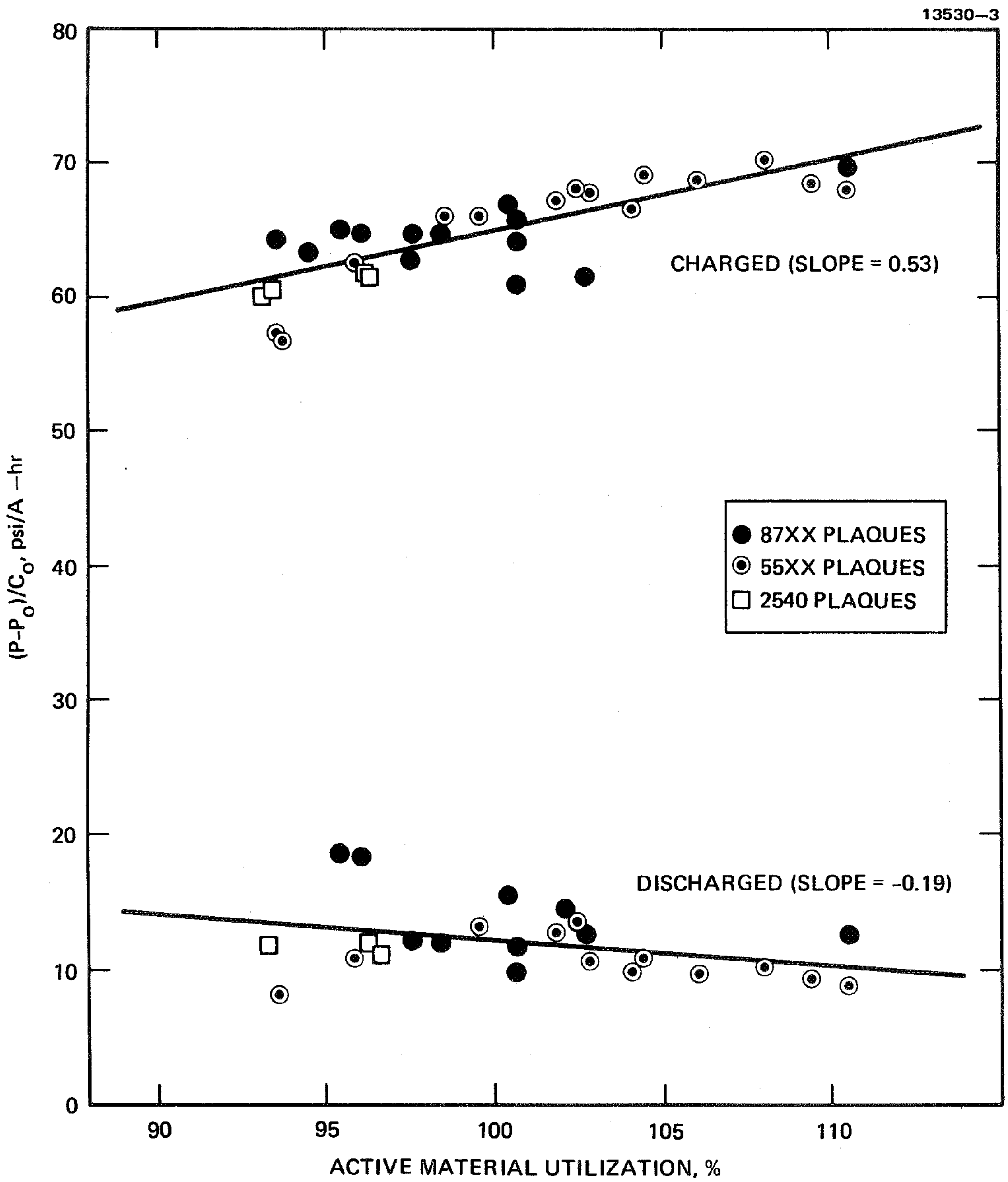

Figure 6. $(P-P_O)/C$ versus active material utilization after 1700 cycles. Charged for 16 hours at 0.1 C rate and discharged to 0.5 V at 0.5 C rate.